Note: In the general case of non-ideal, non-linear (NINL) chromatography, only numerical solutions to the applicable non-linear partial differential equations involved can be found. Several examples are found ref 2, where simulated NINL peaks are compared with INL peaks with the same parameters, except for the diffusion term. It is seen that the NINL peaks are lower, wider and more tailing than the INL peak. With a reasonably efficient column ($N > 5000$ for symmetric peaks), the difference might be neglected for practical purposes.

Thus, even if no explicit equation for the retention volume in the NINL case can be given, Equation (1) is approximately valid also for a NINL peak, the discrepancy depending on the column efficiency.

To measure distribution isotherms by chromatography, the so-called *Elution by Characteristic Point* (*ECP*) method has been suggested. Retention volumes to several points on the curved flank of an experimental peak are measured and related to the solute concentration at those points. The distribution isotherm can then be calculated using Equation (1). The validity of the method depends on the efficiency of the column used for these measurements.

There is no known general way of calculating meaningful peak broadening parameters, such as plate numbers from NINL peaks. As the NINL case in practice is common, this observation is important: The usual equations for the calculation of plate numbers (such as those described in CN 3.10.03) should only be applied to effectively symmetrical peaks.

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12D. Supercritical Fluid Chromatography and Extraction (IUPAC Recommendations 1993)

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Abstract

The report present definitions for the terms and symbols used when supercritical fluids are employed as the liquid phase in chromatography and allied areas including sample extraction. The terms supplement those in the general Nomenclature for Chromatography and includes additional more specific terms.

Introduction

Following the General Assembly Meeting in 1989 the Limited Life Time Commission for Chromatography and Other Analytical Separations took over the work on the nomenclature for chromatography that had previously been undertaken by the Commission for Analytical Nomenclature. A major part of the work was the Nomenclature for Chromatography which had been developed over a number of years by L. S. Ettre and has recently been published [1]. This work was comprehensive and included all the major areas of chromatography. Specialist chapters covered the specific areas of size exclusion chromatography and ion-exchange

chromatography. However, it was clear that as further new areas of separation science were developed specific terminologies of further additional terms and definitions would be needed.

Over the last few years the use of a supercritical fluid as the mobile phase in chromatography has become an accepted routine method. In the Nomenclature for Chromatography Ettre noted (1.4.04) "In general, the terms and definitions used for gas or liquid chromatography are equally applicable to supercritical-fluid chromatography". However, supercritical fluid chromatography has also lead to the use in the literature of a number of new terms whose meanings have been generally adopted by workers in the field. These new terms are formalized in the present Supplement to the general nomenclature of chromatography. Supercritical fluids have also been used for the extraction of samples and frequently similar equipment and operating conditions have been employed and many of the terms are also applicable in this field.

This nomenclature is designed to be used as a supplement to the principal nomenclature paper and is written as Section 7 of that paper [1]. It therefore omits any terms which have already been defined unless a new or additional definition has been necessary. The paper is also complementary to the definitions and terms for supercritical fluid chromatography recently published by ASTM [2].

*7. Special Terminology Used in Supercritical-Fluid Chromatography and Extraction

7.1 Basic Definitions

7.1.1 Critical temperature (T_c) The maximum temperature at which a gas can be converted into a liquid by an increase in pressure.

7.1.2 Critical pressure (p_c) The minimum pressure which would suffice to liquefy a substance at its critical temperature. Above the critical pressure, increasing, the temperature will not cause a fluid to vaporize to give a two-phase system.

7.1.3 Critical point The characteristic temperature (T_c) and pressure (p_c) above which a gas cannot be liquefied.

7.1.4 Supercritical fluid The defined state of a compound, mixture or element above its critical pressure (p_c) and critical temperature (T_c).

7.1.5 Reduced temperature (T_r) The ratio of the temperature (T) in the system to the critical temperature (T_c)

$$T_r = T/T_c$$

7.1.6 Reduced pressure (p_r) The ratio of the pressure in the system (p) to the critical pressure (p_c).

$$p_r = p/p_c$$

7.2 The Mobile Phase

7.2.1 The *mobile phase* was defined previously in 1.1.06

7.2.2 Mobile-phase pressure

7.2.2.1 Outlet pressure (p_o) Defined as in 3.6.02.2. However, unlike gas and liquid chromatography the outlet pressure in supercritical-fluid chromatography has to be maintained above ambient pressure by a flow restrictor (7.3.1) or back-pressure regulator (7.3.2).

7.2.2.2 Pressure drop across the column (Δp) Defined as 3.6.02.3.

*For Sections 1–6 see *Pure & Appl. Chem.*, Vol. 65, No. 4, pp. 819–872, 1993.

7.2.3 Mobile-phase volume flow rate. Defined as 3.6.04. In supercritical-fluid chromatography this is usually quoted as the rate of delivery of the pumping system.

7.2.4 Mobile-phase mass flow rate The rate of mass flow through the column. It is usually determined by measuring the gas-flow rate (or liquid-flow rate) at ambient conditions after the mobile phase has been depressurized. If liquid modifiers are present in the mobile phase, corrections will be needed.

7.2.5 Mobile-phase composition The composition of the mobile-phase which is delivered to the column. This should be described in such a way that it can be reproduced in different laboratories. It can be expressed on a mass, volume, or mole fraction basis but in each case the temperature and pressure must also be defined.

If the individual components are pumped separately, the relative delivery flow rates should be defined.

Premixed eluents are often used and can be defined by their mass composition as recorded by the manufacturer. However, the delivered composition may depend on the relative volatility of the components and can change as a function of syringe pump volume and time.

7.2.5.1 Mobile-phase modifier Modifiers are materials (usually organic compounds such as methanol or acetonitrile) added to the supercritical fluid being used as the mobile phase to alter the elution properties.

7.3 Instrumentation

Most of the components of the instrumentation for supercritical-fluid chromatography are in common with liquid and gas chromatography and are defined in **Section 2.1** Apparatus for Column Chromatography.

7.3.1 Flow restrictor This is a device which restricts the flow of the mobile phase leaving the column and is used to maintain the pressure in the chromatographic column.

7.3.1.1 Capillary restrictor This is a capillary tube which may be tapered or constricted and acts as a mass-flow controller. The column pressure is controlled by adjusting the pump flow rate.

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7.3.1.2 Frit restrictor A frit placed at the end of an open-tubular column to act as a flow restrictor. Sometimes referred to as an *integral frit restrictor*.

7.3.2 Back-pressure regulator This is a device which is placed after the column and is used to regulate the pressure in the column by a pressure-adjustable diaphragm or controlled nozzle so that the same column-outlet pressure is maintained irrespective of the mobile-phase pump flow rate.

7.3.3 Sample injector as defined in 2.1.02. The most common form in supercritical-fluid chromatography is the *bypass injector* (see 2.1.02.2). In capillary supercritical-fluid chromatography a *timed injector* is often used.

7.3.3.1 Timed injector This is a form of *bypass injector* in which the rotation of the valve is timed so that only a portion of the contents of the sample loop can pass to the column.

7.3.4 High-pressure flow cell A flow-through cell (usually spectroscopic) designed for use at high pressures so that the sample remains dissolved in the mobile phase during detection.

7.4 The Chromatographic Medium

Supercritical-fluid chromatographic separations are carried out using capillary columns or packed columns similar to those used in gas or liquid chromatography (see **Section 3.1**). Stationary phases are usually chemically bonded to the support. Non-chemically bonded phases are often unsuitable as the stationary phase may be soluble in the mobile phase.

7.5 Terms Related to the Chromatographic Process

7.5.1 Isobaric separation Chromatographic separation carried out using constant inlet and outlet pressure conditions.

7.5.2 Isopycnic separation Chromatographic separations carried out using constant density conditions. The temperature and pressure may be altered during the run (originally the term *isoconfertic separation* was used but this term is not recommended).

7.5.3 Programmed elution A procedure is which the conditions of the separation are changed in a programmed manner. Unlike gas or liquid chromatography both the pressure and temperature can be programmed.

The term "*gradient elution*" should be restricted to changes in composition of the mobile phase with time (see 1.6.04).

7.5.3.1 Density-programmed elution A separation carried out using a pressure and/or temperature programme so that the density of the mobile phase changes with time in a pre-determined manner during the separation.

7.5.3.2 Pressure-programmed elution A separation carried out using a programmed increasing pressure with time.

7.5.3.3 Pressure/temperature-programmed elution A separation carried out using conditions where the pressure and temperature are programmed simultaneously. The temperature may be programmed to increase or decrease.

7.6 Coupled-systems

As well as discrete chromatographic detectors, supercritical-fluid chromatography has been coupled to more complex detectors and to other separation techniques and the most widely used are listed here.

7.6.1 Coupled supercritical-fluid chromatography-mass spectrometry (SFC-MS) Separation system in which the column effluent from a supercritical-fluid chromatograph is passed directly to the inlet chamber of a mass spectrometer.

7.6.2 Coupled supercritical-fluid chromatography-Fourier-transform infrared spectrometry (SFC-FTIR) Separation system in which the column effluent from a supercritical-fluid chromatograph is passed directly through a Fourier-transform infrared specrometer.

7.6.3 Coupled supercritical-fluid chromatography-gas chromatography (SFC-GC) Separation system in which a fraction from the supercritical-fluid chromatograph effluent is transferred directly to the inlet port or column of a gas chromatograph system.

7.7 Supercritical-fluid Extraction

7.7.1 Supercritical-fluid extraction (SFE) Extraction of a material using a supercritical fluid. The extracted material is usually recovered by reducing the temperature or pressure of the extraction fluid and allowing the volatile components of the mobile phase to evaporate. Instrumentally supercritical-fluid extraction can use many of the components of a supercritical-fluid chromatographic system. It can used either as an on-line sample introduction method for a chromatographic separation or as an off-line sample preparation method.

7.7.2 Coupled supercritical-fluid extraction-supercritical-fluid chromatography (SFE-SFC) System in which a sample is extracted with a supercritical-fluid which then places the extracted material in the inlet port of a supercritical-fluid-chromatographic system. The extract is then chromatographed directly using a supercritical fluid.

7.7.3 Coupled supercritical-fluid extraction-gas chromatography (SFE-GC) and Coupled supercritical-fluid chromatography-liquid chromatography (SFE-LC) System in which a sample is extracted using a supercritical fluid which is then depressurized to deposit the extracted material in the inlet port or column of a gas or liquid chromatographic system, respectively. The extract is then chromatograped directly.

Table 1 Index of additional terms

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Table 2 List of symbols

p_c	Critical pressure	7.1.2
T_c	Critical temperature	7.1.1
p_r	Reduced pressure	7.1.6
T_r	Reduced temperature	7.1.5

Table 3 List of acronyms

SFE	Supercritical-fluid extraction
SFC-FTIR	Supercritical-fluid chromatography-Fourier transform infrared spectroscopy
SFC-GC	Supercritical-fluid chromatography-gas chromatography
SFC-LC	Supercritical-fluid chromatography-liquid chromatography
SFC-MS	Supercritical-fluid chromatography-mass spectrometry
SFE-GC	Supercritical-fluid extraction-gas chromatography
SFE-LC	Supercritical-fluid extraction-liquid chromatography
SFE-SFC	Supercritical-fluid extraction-supercritical-fluid chromatography

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